



# Atomic Layer Deposition (ALD) - An Enabling Technology for NASA Space Systems

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# What is a Thin Film?



**Thin film:** thickness typically  $<1000\text{nm}$ .

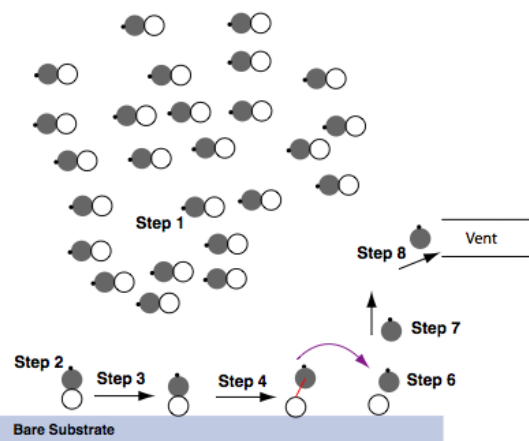
**Special properties of thin films:** different from bulk materials, it may be –

- Not fully dense
- Under stress
- Different defect structures from bulk
- Quasi - two dimensional (very thin films)
- Strongly influenced by surface and interface effects

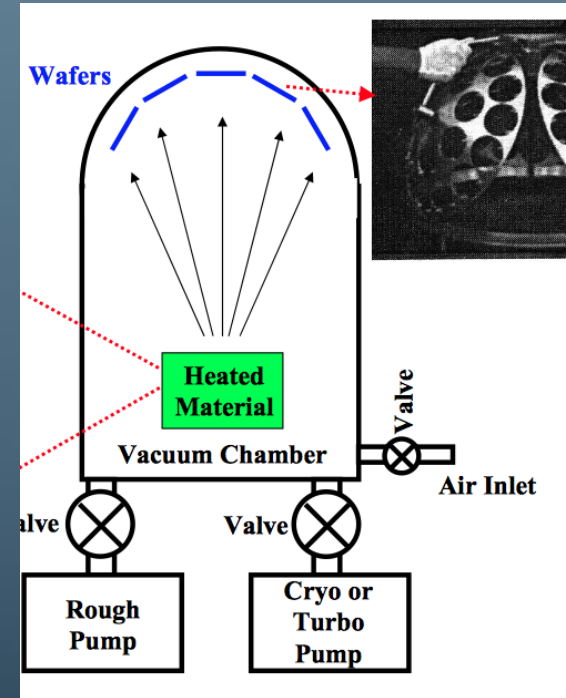
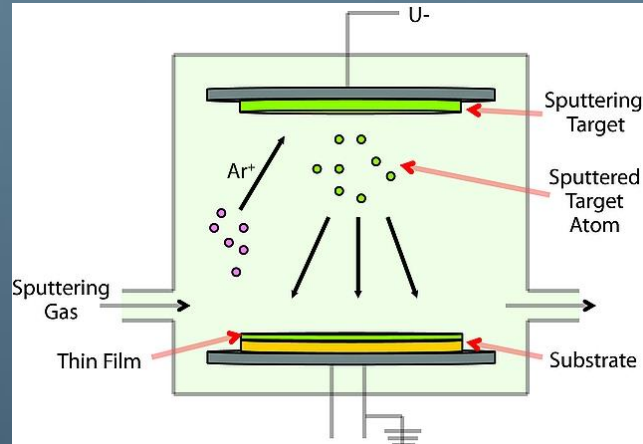
# Other Deposition Techniques



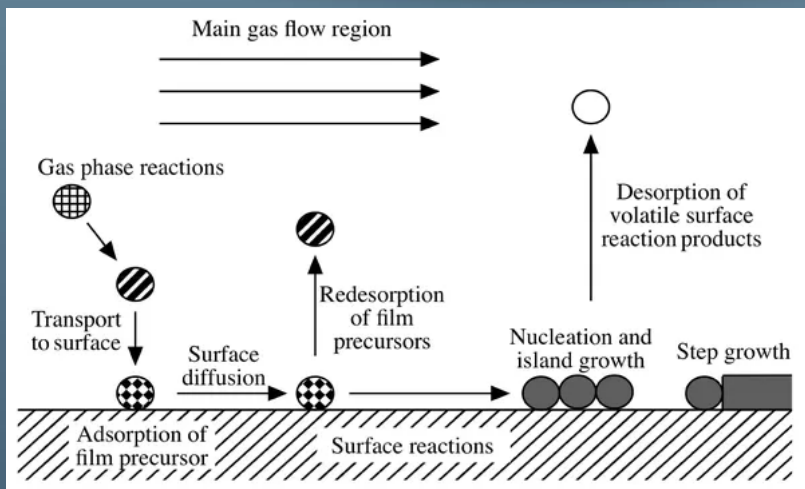
CVD Process



1. Precursor gas phase reaction
2. Diffusion
3. Adsorption
4. Surface Process
5. Desorption
6. Diffusion
7. Purge

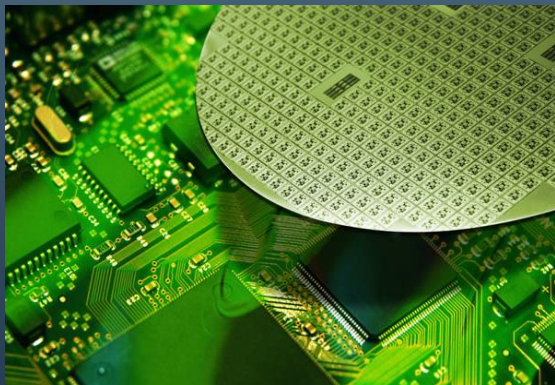


# Thin-Film Engineering



Vapor-phase deposition of inorganic materials

Microelectronics



James River Semiconductor

Solar energy



First Solar

Solid-state lighting



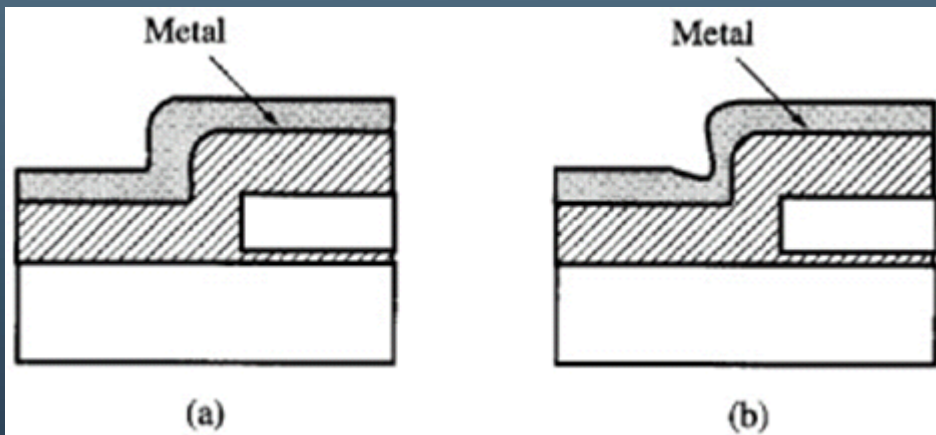
The New Ecologist

# Common Denominator



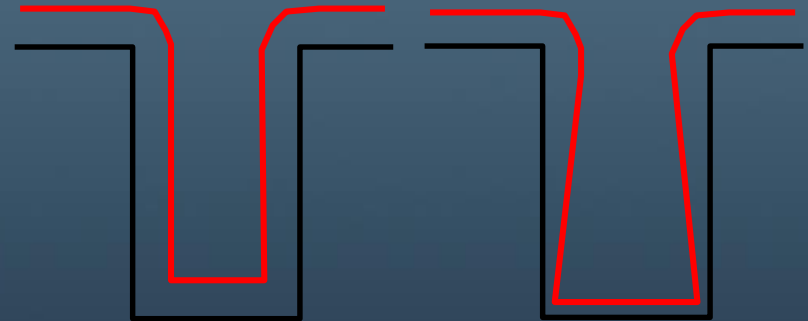
- Deposition only occurs on substrates that “see” the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

## Step Coverage Example



conformal

non-conformal



Step coverage of metal over non-planar topography.

(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.

(b) Poor step coverage, here thinner for vertical surfaces.



# Atomic Layer Deposition



Atomic  
Layer  
Deposition

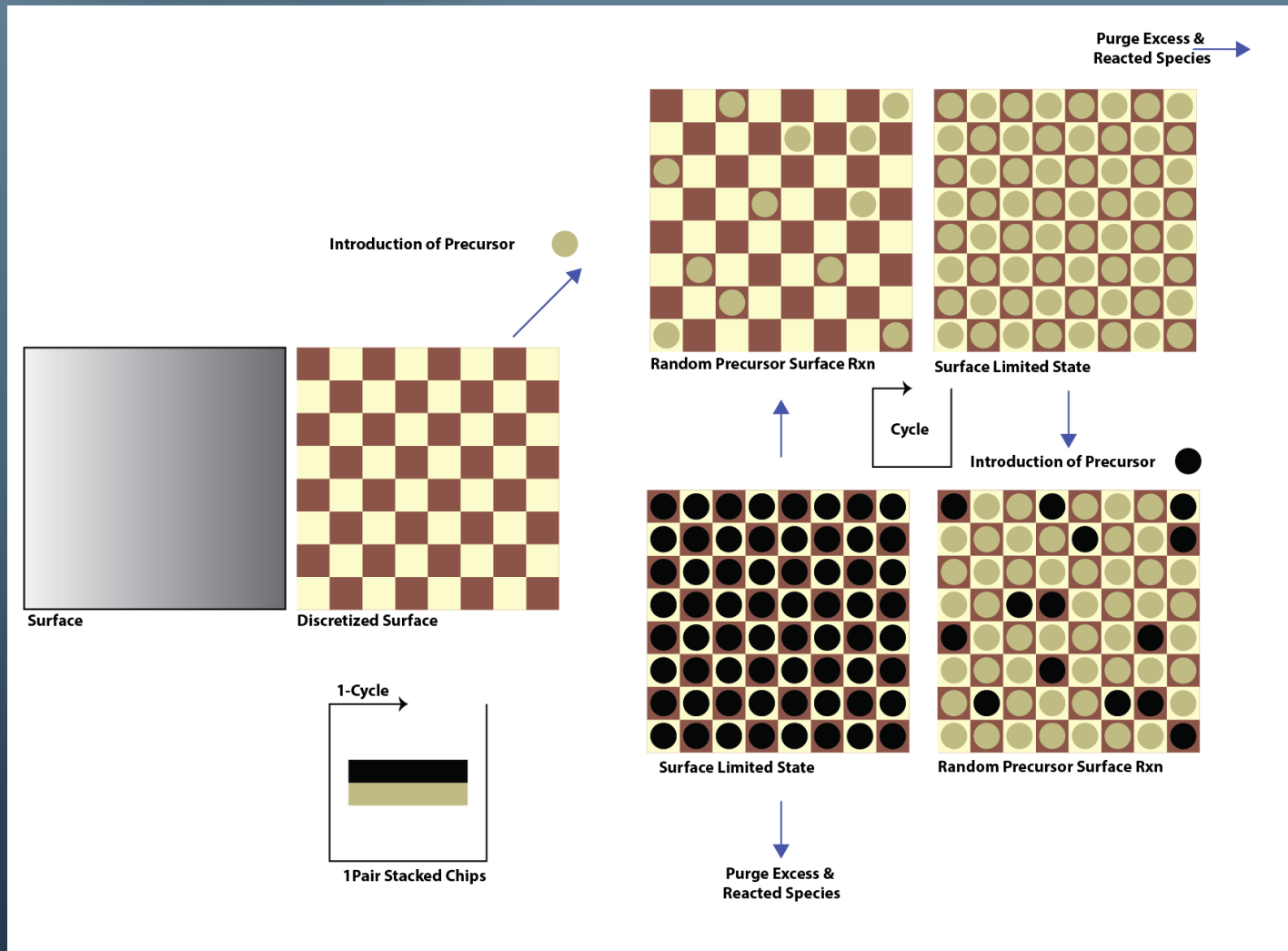


A thin film “nanomanufacturing” tool that allows for the conformal coating of materials on a myriad of surfaces with precise atomic thickness control.

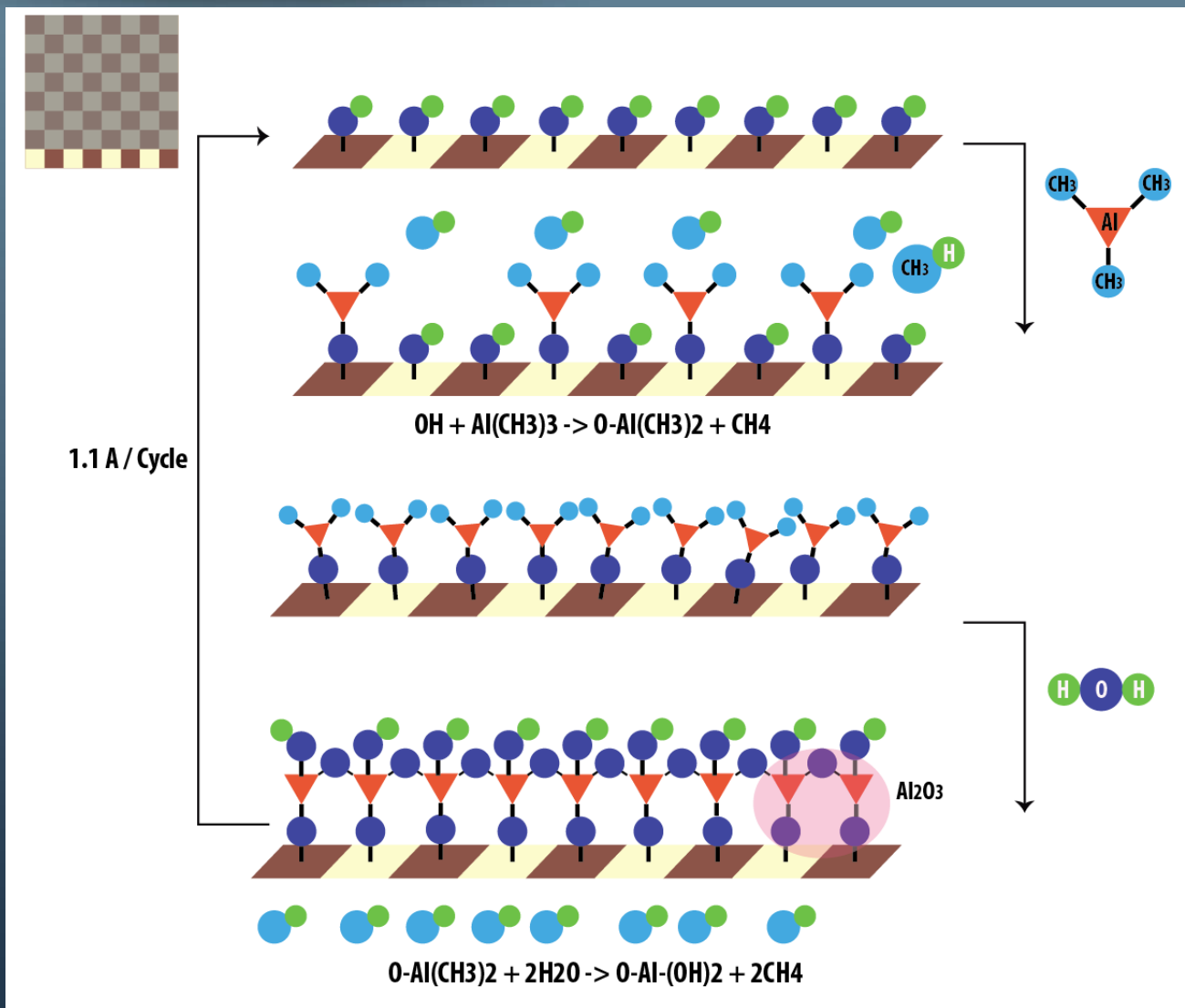
Based on:

- Paired gas surface reaction chemistries
- Benign non-destructive temperature and pressure environment
  - Room temperature -> 250 °C (even lower around 45 °C)
  - Vacuum

# ALD Analogy (Checkers)



# ALD Analogy Chemistry



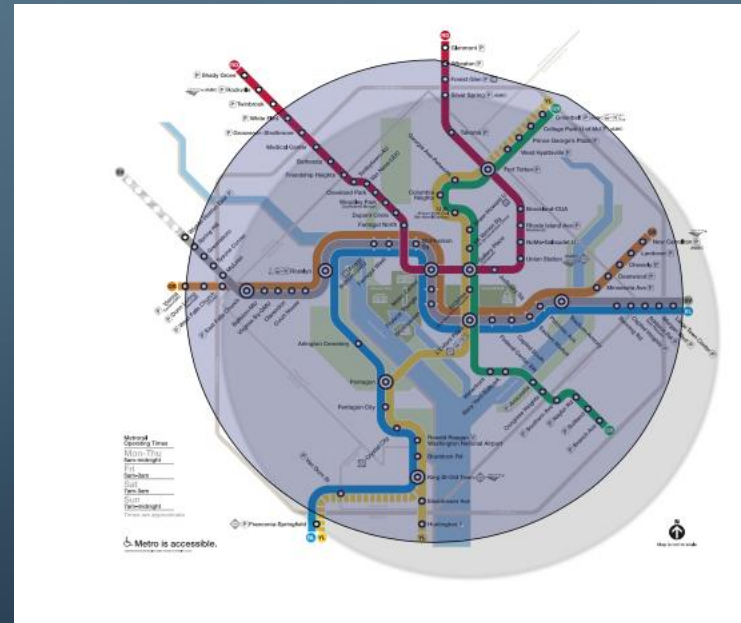
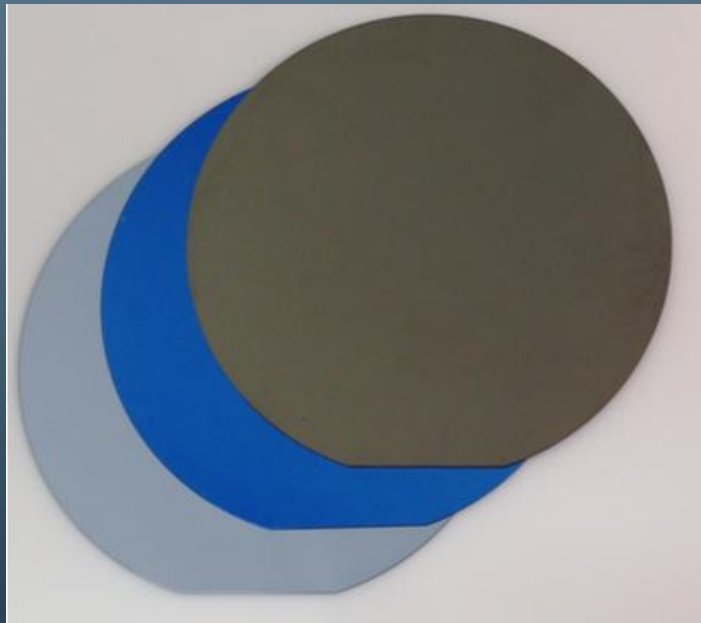


# ALD

Precursor A + Precursor B  $\rightarrow$  Solid film + Gas by-products

Cyclic operation: A  $\rightarrow$  purge  $\rightarrow$  B  $\rightarrow$  purge  $\rightarrow$  A  $\rightarrow$  purge  $\rightarrow$  ...

Atomic-level thickness control ...

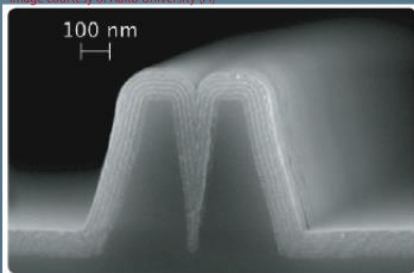


... equivalent to a 60  $\mu\text{m}$  layer over a city-sized wafer

# ALD Advantageous Property

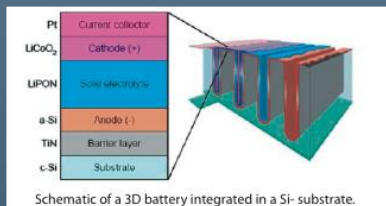


Artificial trench filled with an ALD nanolaminate  
Image courtesy of Aalto University (F3)



## Epitaxial Growth

Multilayer consisting of:  
Al<sub>2</sub>O<sub>3</sub> - 25 nm  
TiN - 20 nm  
Al<sub>2</sub>O<sub>3</sub> - 25 nm  
Dr. Fred Roozeboom, NXP Semiconductors Research and  
Dr. Erwin Kessels, University of Technology, Eindhoven



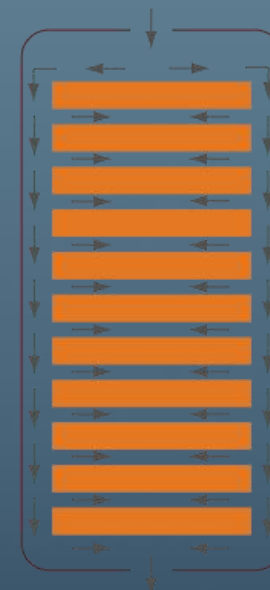
Schematic of a 3D battery integrated in a Si-substrate.  
The cross-section shows the various functional layers  
in the battery stack as well as the candidate materials.

Kanops, H.C.M. et al., ECS Trans., 25 (2009) pp. 313-344

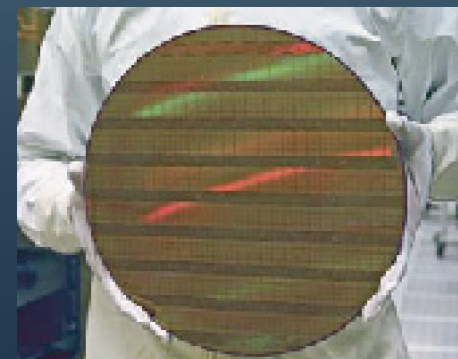
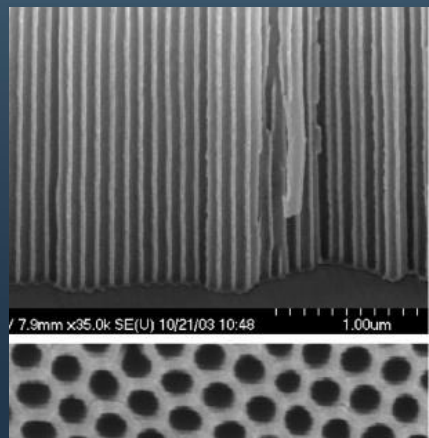
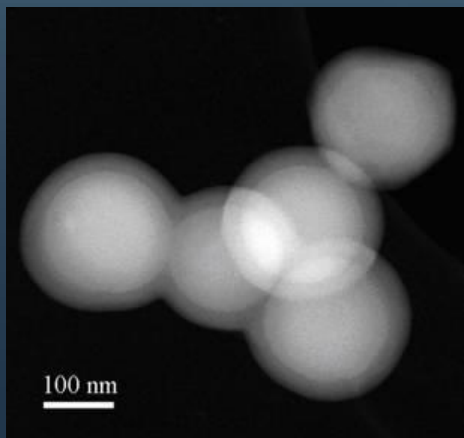
## Batch Process



Coating Silver with Aluminum Oxide  
<http://www.glassonweb.com/>



## Substrate Independence



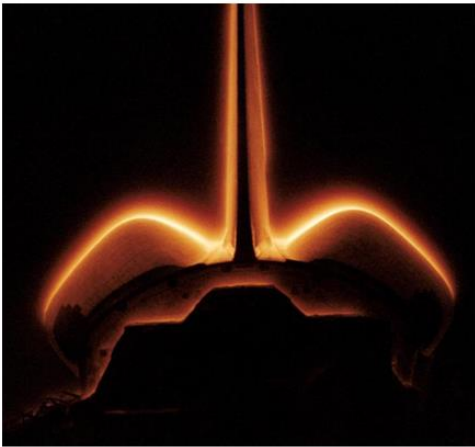
Goddard  
Space Flight Center

# ALD Material Systems

H 1	<div><div>O:Oxide N:Nitride M:Metal P:Phosphide/Asenide S:Sulphide/Selenide/Telluride</div><div>C:Carbide F:Fluoride D:Dopant</div></div>																He 2														
<div>O</div> Li 3	Be 4																	<div>O</div> N B 5 D	C 6	N 7	O 8	F 9	Ne 10								
Na 11	<div>O</div> Mg 12 F	<div><div>O</div>Oxide of this element has been deposited by the ALD community</div> <div><div>O</div>Recipe for this material is available from CNT staff or customer base</div>																<div>O</div> N M P Al 13 D	<div>O</div> N M C Si 14	P 15	S 16	Cl 17	Ar 18								
K 19	<div>O</div> Ca 20 S F	<div>O</div> Sc 21	<div>O</div> N M Ti 22 S	<div>O</div> V 23	<div>O</div> Cr 24	<div>O</div> N M Mn 25 S D	<div>O</div> N M Fe 26	<div>O</div> N M Co 27	<div>O</div> N M Ni 28	<div>O</div> N M Cu 29 S D	<div>O</div> Zn 30 S F D	<div>O</div> N P Ga 31 D	<div>O</div> N M Ge 32	As 33	Se 34	Br 35	Kr 36														
Rb 37	<div>O</div> Sr 38 S F	<div>O</div> Y 39	<div>O</div> N Zr 40	<div>O</div> N Nb 41	<div>O</div> N M Mo 42	Tc 43	<div>O</div> M Ru 44	<div>O</div> M Rh 45	<div>O</div> M Pd 46	<div>O</div> M Ag 47	<div>O</div> S Cd 48	<div>O</div> N P In 49 S	<div>O</div> S Sn 50 S D	<div>O</div> M Sb 51 D	Te 52	I 53	Xe 54														
Cs 55	<div>O</div> Ba 56 S	<div>O</div> La 57 S F	<div>O</div> N Hf 72 S F	<div>O</div> N M Ta 73 C	<div>O</div> N M W 74	<div>O</div> Re 75	<div>O</div> Os 76	<div>O</div> M Ir 77	<div>O</div> M Pt 78	Au 79	<div>O</div> S Hg 80	Tl 81	<div>O</div> S Pb 82 D	<div>O</div> Bi 83	Po 84	At 85	Rn 86														
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109																							
																		<div>O</div> Ce 58 D	<div>O</div> Pr 59	Nd 60	Pm 61	<div>O</div> Sm 62	<div>O</div> Eu 63 D	<div>O</div> Gd 64	<div>O</div> Tb 65 D	<div>O</div> Dy 66	<div>O</div> Ho 67	<div>O</div> Er 68	<div>O</div> Tm 69 D	<div>O</div> Yb 70	<div>O</div> Lu 71
																		Th 90	Pa 92	U 93	Np 94	Pu 95	Am 96	Cm 97	Bk 98	Cf 100	Es 101	Fm 102	Md 104	No 4	Lr 4

- Gordon, Roy (2008). Atomic Layer Deposition (ALD): An Enable for Nanoscience and Nanotechnology. PowerPoint lecture presented at Harvard University, Cambridge, MA.
- Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory

# NASA Impacts



NASA STS-062; *Nature*, 354 (1991)

ISS Orbit 400 km  
Atomic O Density =  $1 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$   
 $v = 7.2 \times 10^5 \text{ cm s}^{-1}$   
→ 1 O impact  $\text{nm}^{-2} \text{ s}^{-1}$   
KE = 4.2 eV

## Alumina ALD on Kapton substrate

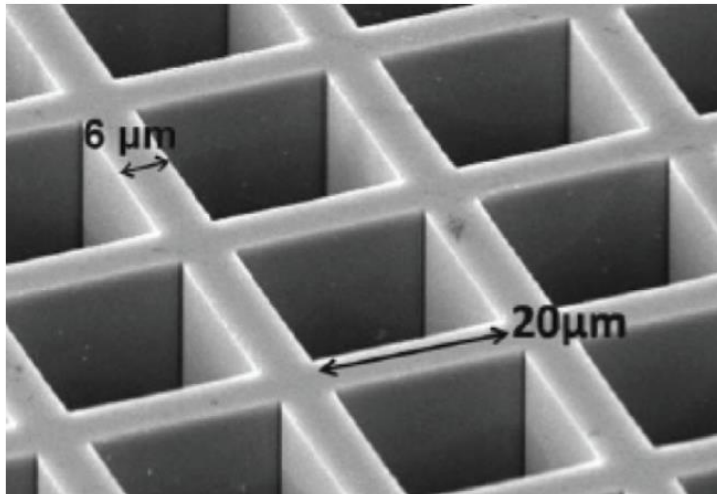


- Conformal, flexible,  $\mathcal{O}(100 \text{ nm})$ , **nonvolatile oxide** coating
- Low temperature ( $100^\circ\text{C}$ ) deposition process

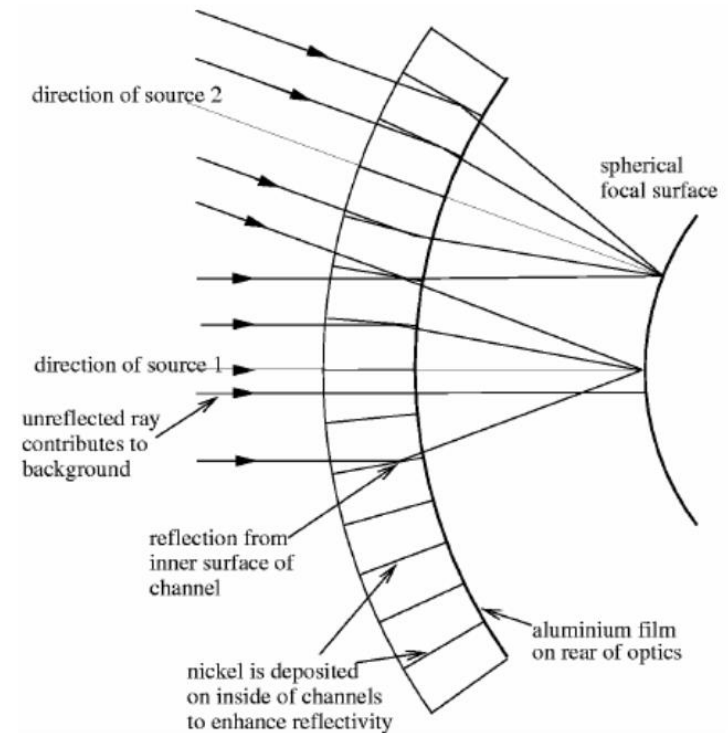




# STORM XRI

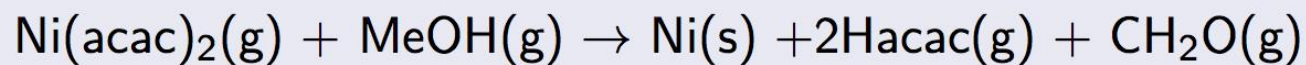


NASA GSFC

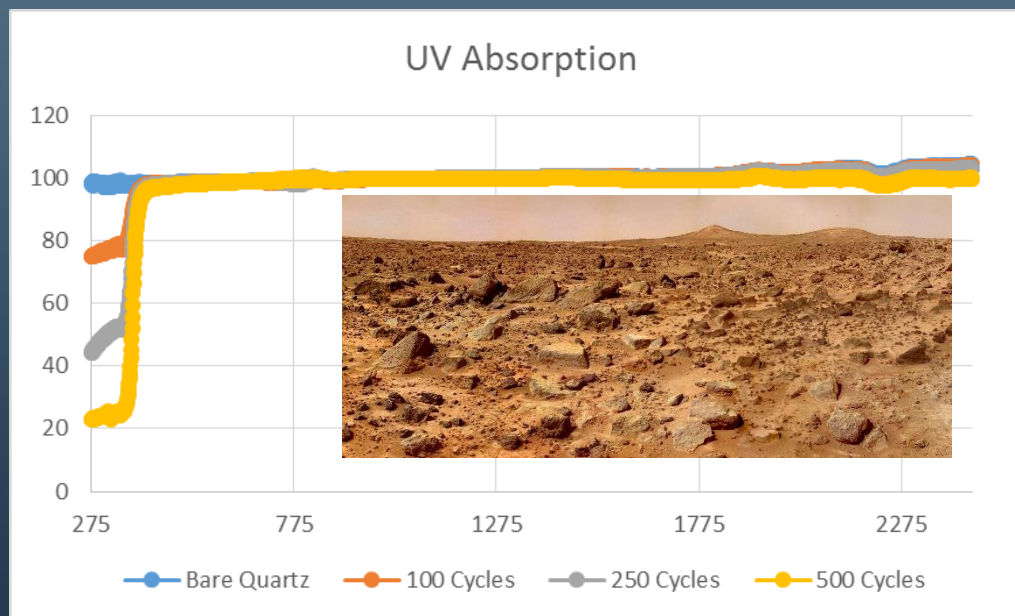
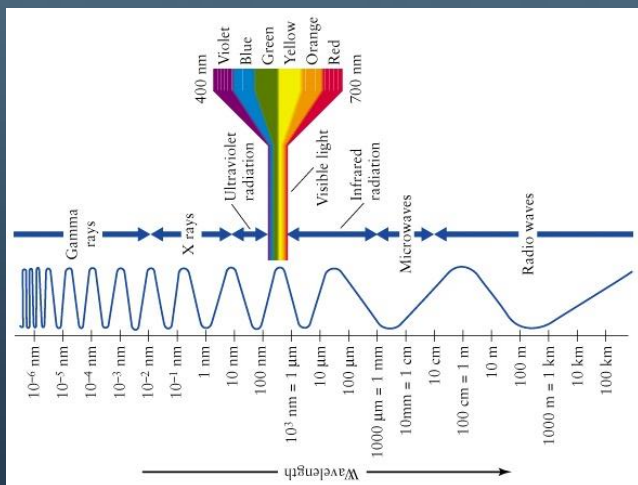
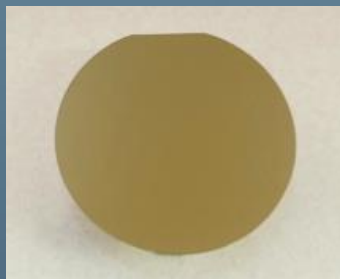
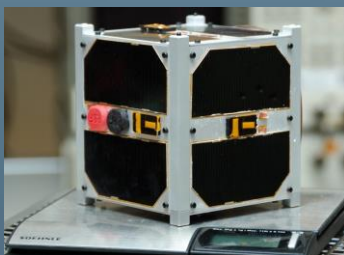


Black et al. 2003, arXiv

## Ni ALD

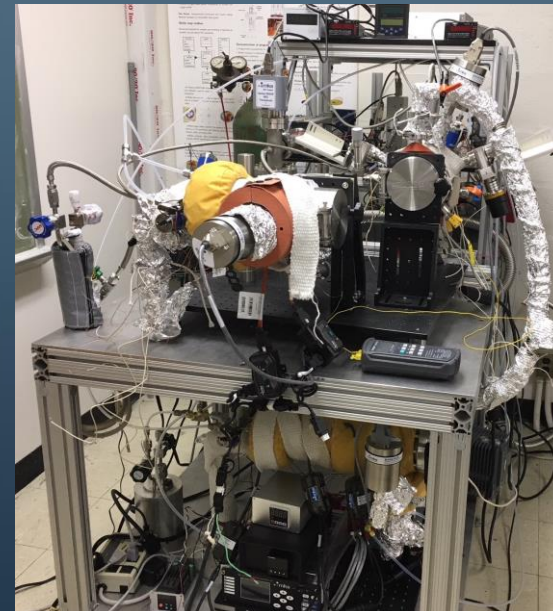
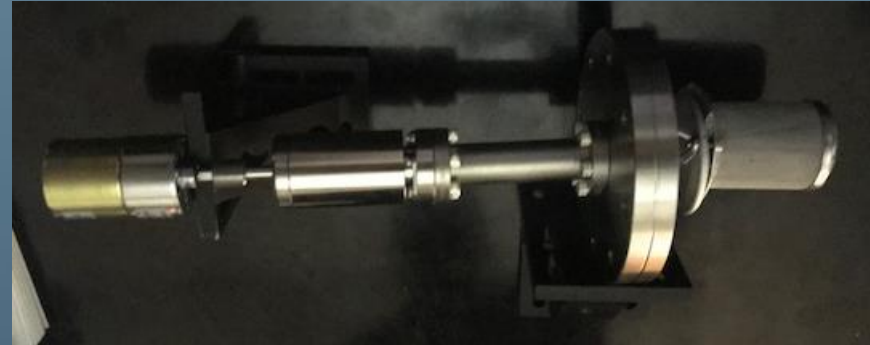
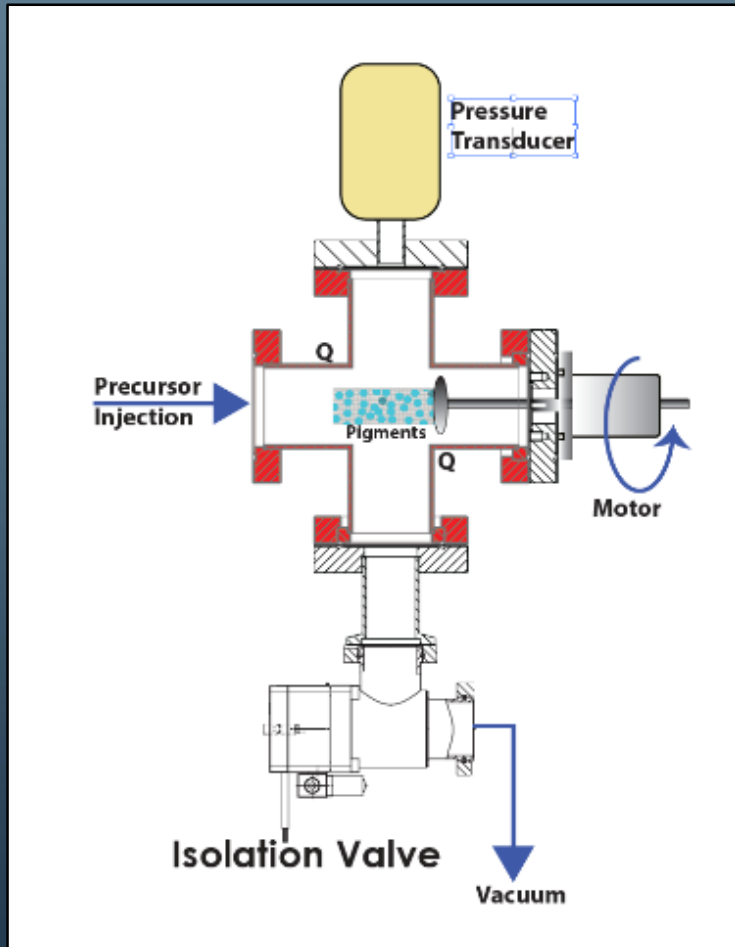


# ZnO





# ALD For Radiators - Pigments





# Problem

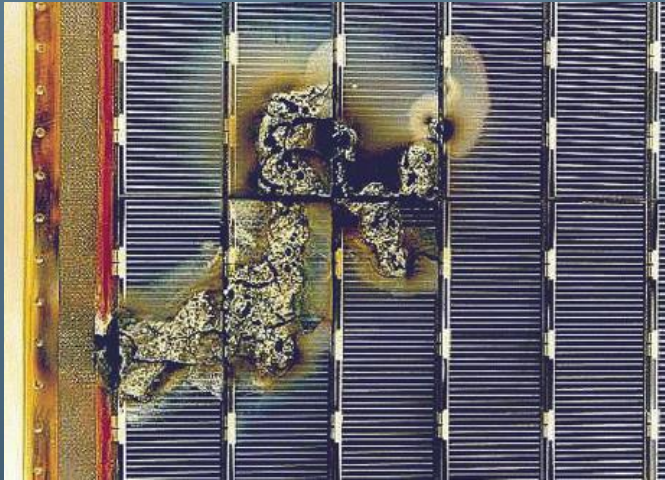
Spacecraft charging is the condition that occurs when a spacecraft accumulates excess electrons or ions. For a conducting spacecraft, the excess charges are on the surface. The term spacecraft surface charging (absolute charging) is used to clearly denote charging on the spacecraft surface as opposed to other charge distributions such as the voltage differences between electrically isolated parts of the spacecraft (differential charging).

## HAZARD

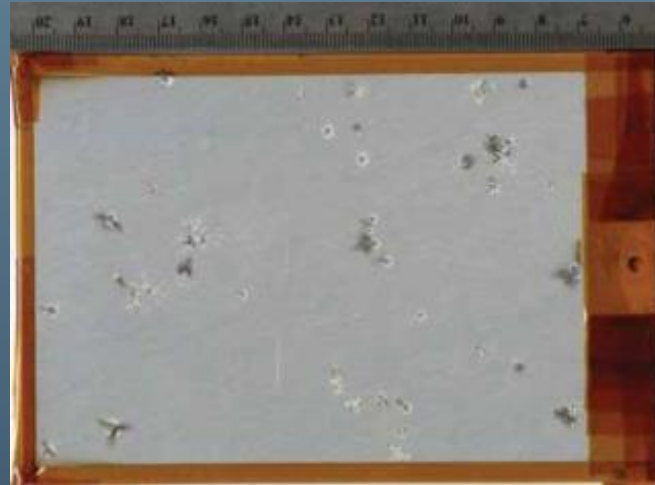
If a charge builds up that is too big for the spacecraft's material to hold, discharge arcs, which are essentially strong electrical currents, will occur.

And depending on where those arcs go, they can damage electronic components, destroy sensors, or damage important materials such as thermal control coatings.

# Problem



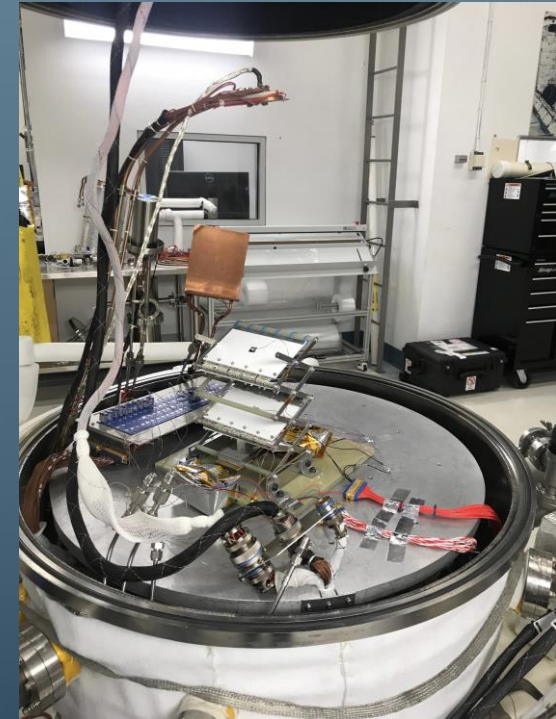
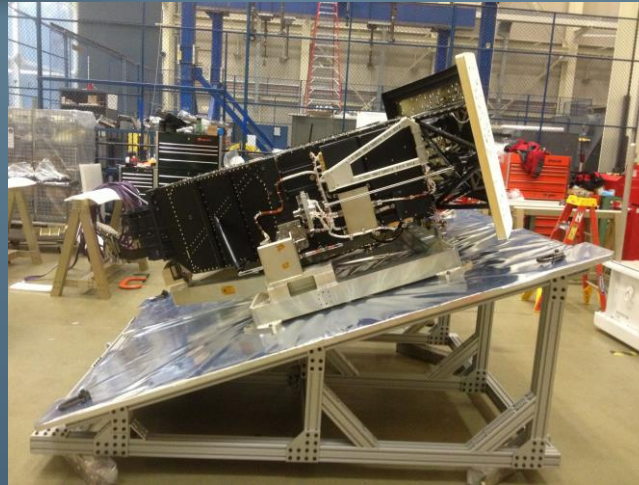
ESA EURECA satellite solar array sustained arc damage.  
Credits: ESA



Arc damage in laboratory tests of the chromic acid anodized thermal control coating covering ISS orbital debris shields.  
Credits: NASA/T. Schneider



# Radiator - Vary in Size



Origami Inspired



The space station's radiator system, which is a critical component of the active system, consists of seven panels (each about 6 by 12 feet)



Wide Field Planetary Camera 2 (WFPC2) that was installed on the Hubble Space Telescope in December 1993, and removed during the last servicing mission in 2009



# Motivation

- Most white pigments do not dissipate electrical charge without a dopant or additive
- Two most commonly used dissipative thermal coatings (Z93C55 and AZ2000) rely on indium hydroxide or tin oxide as charge dissipative additives utilizing sol gel wet chemistry
- ITO formed locally on a macroscopic scale due to seeding and ITO crystal formation on the boundaries of the pigment grains. Thickness and dispersion throughout the coating are difficult to control.

Instead of postprocessing the dissipative coating can we preprocess the dissipative coating before binding directly on the pigment itself?

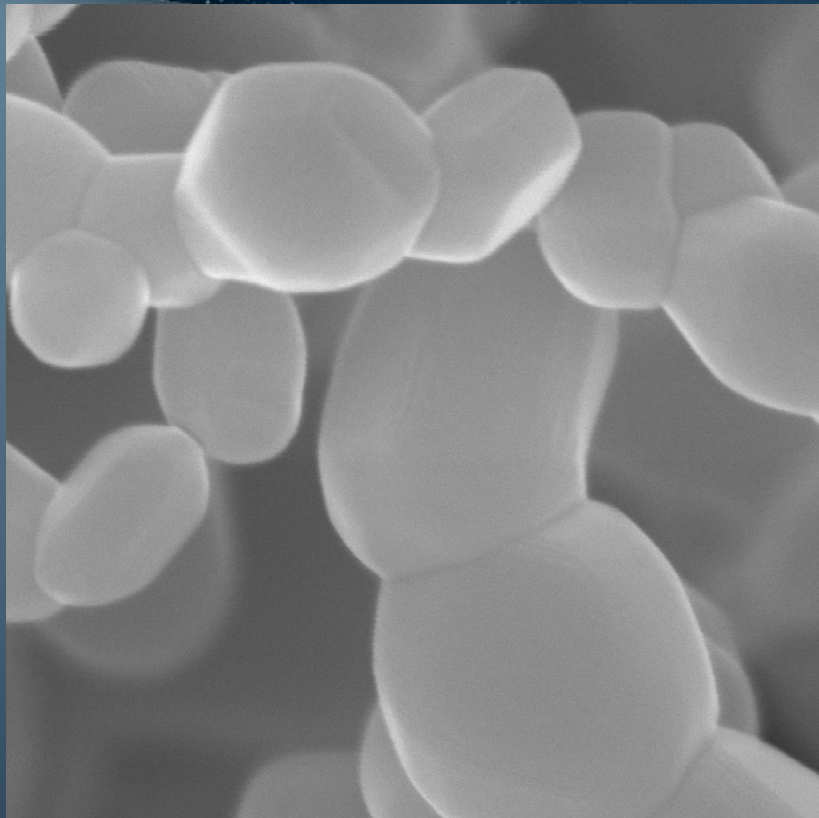


# Experimental Procedures

- The first set of experiments were conducted on flat substrates for the ALD of  $\text{In}_2\text{O}_3$  and ITO, the films were deposited on a variety of substrates including n-type Si(100) wafers for thickness measurements and glass microscope slides for sheet resistivity determination.
- The  $\text{In}_2\text{O}_3$  ALD on the particle substrates was applied to Z93P pigments provided by Alion Science and Technology; these particles had a mean size of 2 microns.
- Thickness and conformity of the ALD films on the Si wafers of  $\text{In}_2\text{O}_3$  and ITO were measured using a J.A. Woollam M-2000D Spectroscopic Ellipsometer. The sheet resistivity of the ALD films on the microscope glass substrates was measured using a Lucas Signatone S-302 four-point probe
- The bulk resistivity of the ALD deposited pigment system is measured in air after the formation of a pellet of 1 in. diameter and a thickness of approximately .5 in. The pigment is compressed lightly by hand and held in place by a 3D printed electrically insulating hollow nylon/Teflon annulus spacer held on an aluminum plate. Resistivity was measured in air and vacuum.

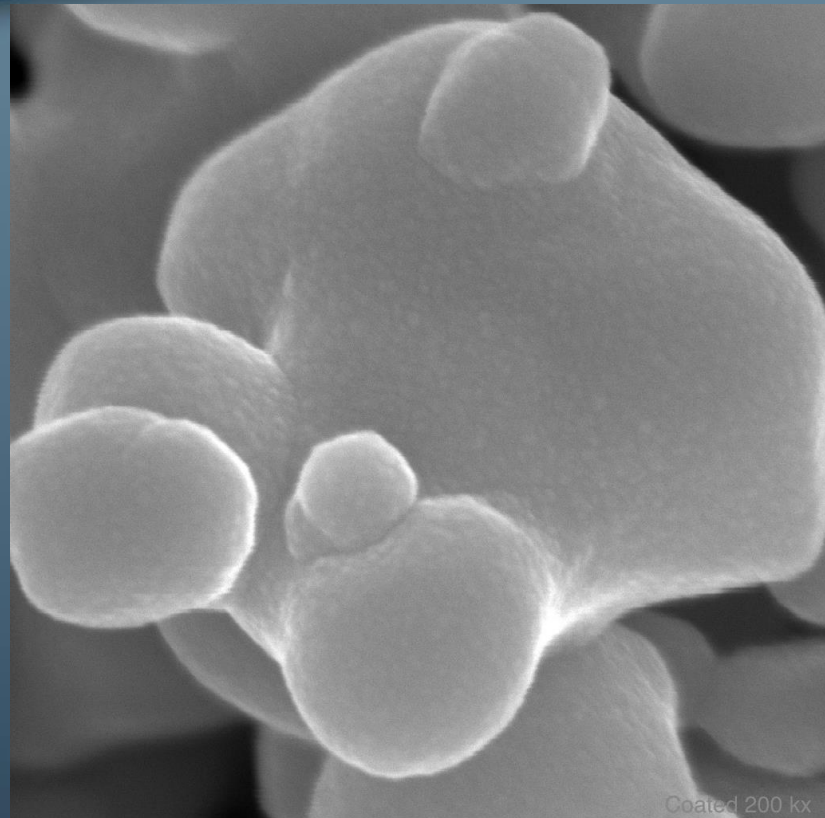


# Results



SEM HV: 15.0 kV	Det: In-Beam SE		XEIA3 TESCAN
WD: 4.93 mm	SEM MAG: 200 kx	200 nm	Uncoated 200 kx
View field: 1.38 $\mu$ m	Date(m/d/y): 10/12/18	University of Maryland AIM Lab	

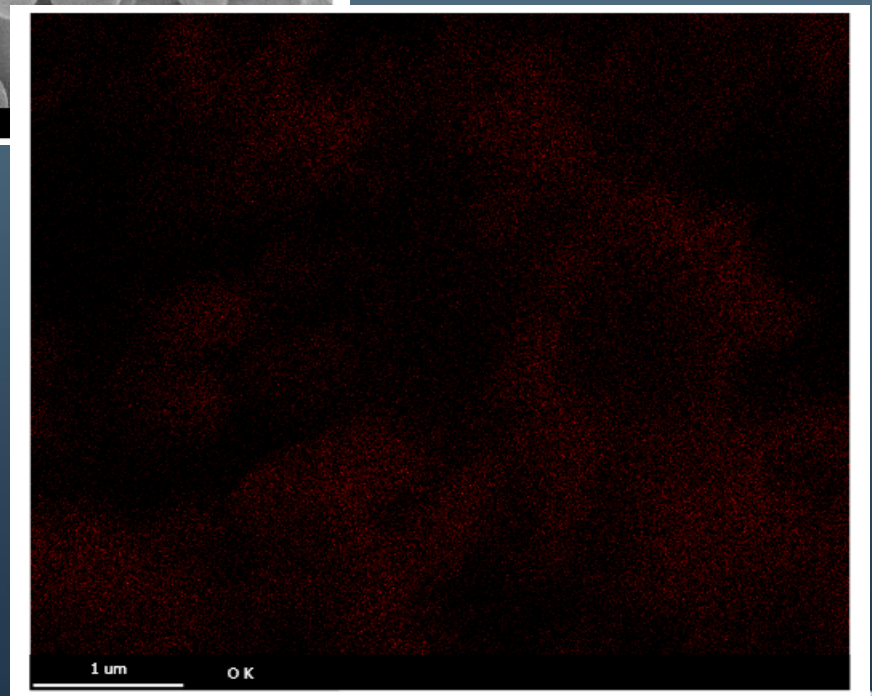
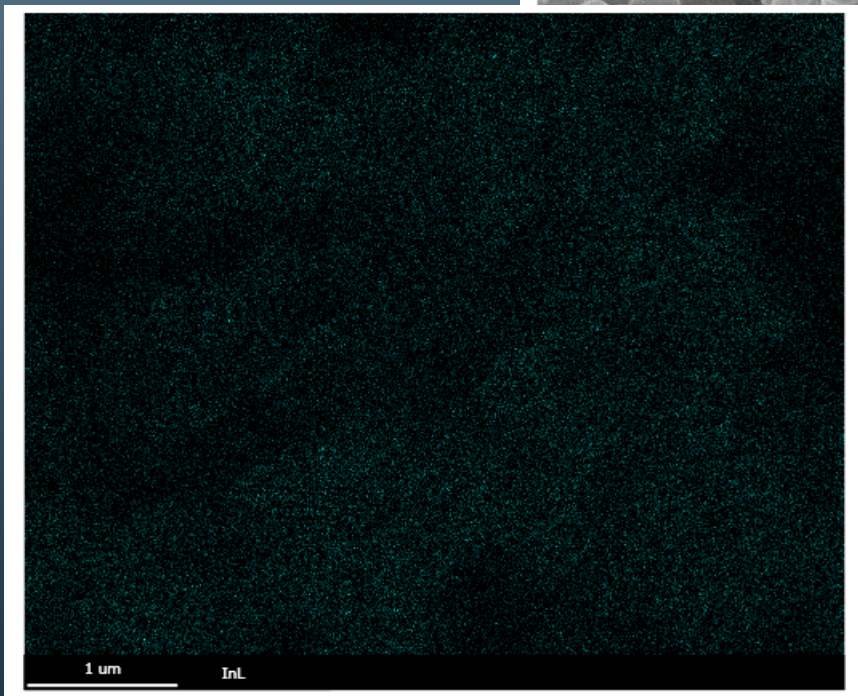
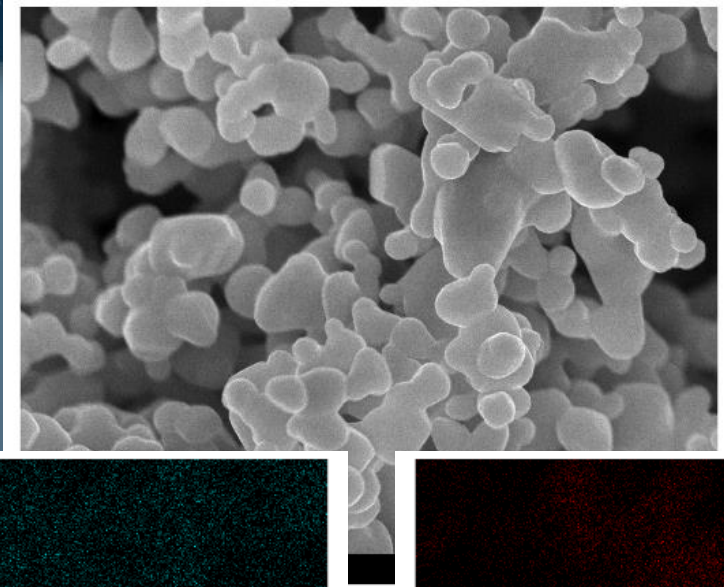
**Uncoated Pigment**



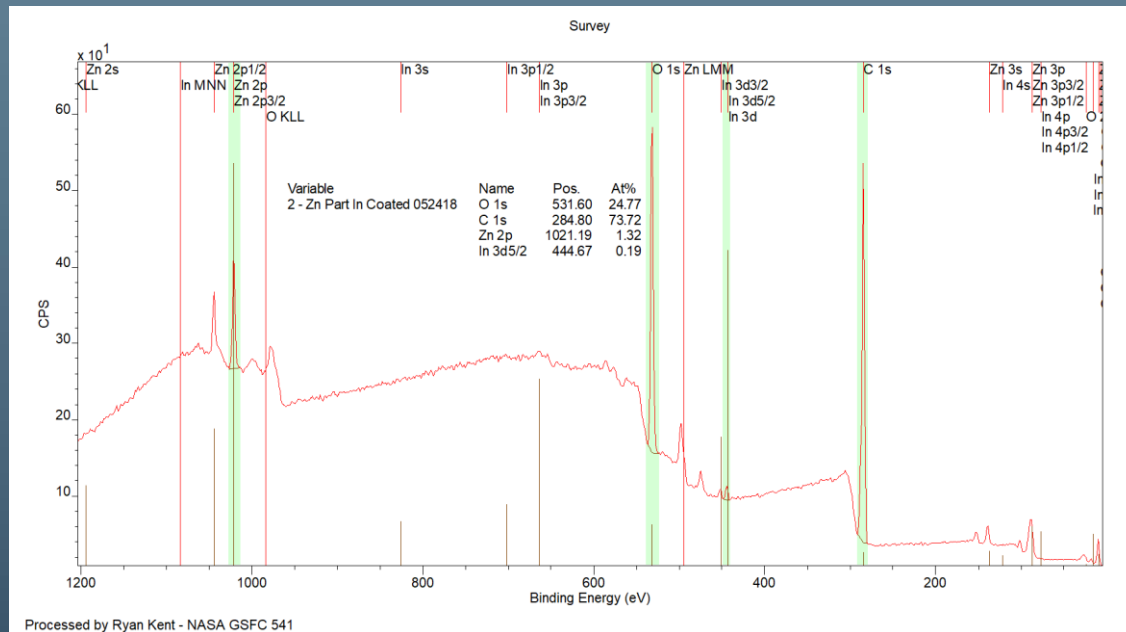
SEM HV: 15.0 kV	Det: In-Beam SE		XEIA3 TESCAN
WD: 5.00 mm	SEM MAG: 200 kx	200 nm	Coated 200 kx
View field: 1.38 $\mu$ m	Date(m/d/y): 10/12/18	University of Maryland AIM Lab	

**Coated Pigment**

# Results



# Results



Spectrum Label	Zinc Oxide Particles	Indium Oxide Coated
C	57.73	73.72
O	33.23	24.76
Zn	9.04	1.28
In	-	0.23

## XPS of Particle Composition



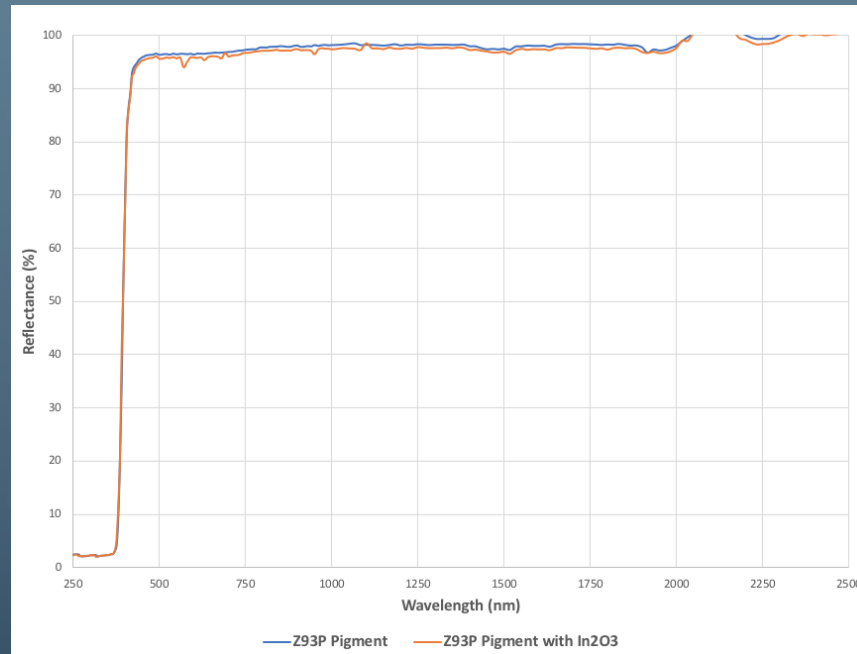
# Results



Pressure (Torr)	Sample	Voltage (V)	R (ohms)
7.60E+02	In <sub>2</sub> O <sub>3</sub> ALD Z93	40	1.30E+08
	Z93	40	5.10E+08
7.00E+01	In <sub>2</sub> O <sub>3</sub> ALD Z93	40	1.60E+08
	Z93	40	8.00E+10
7.00E-02	In <sub>2</sub> O <sub>3</sub> ALD Z93	40	1.80E+08
	Z93	40	1.80E+11
6.00E-02	In <sub>2</sub> O <sub>3</sub> ALD Z93	100	7.00E+07
	Z93	100	6.00E+10

As vacuum is increased the resistivity of the Z93 pigment powders increases several orders of magnitude while the indium oxide treated Z93P pigment remains relatively stable. This increase in resistivity can be attributed to either the removal of moisture within the bulk powder or the compression of the powder filling the void space allowing for an increased number of conduction paths.

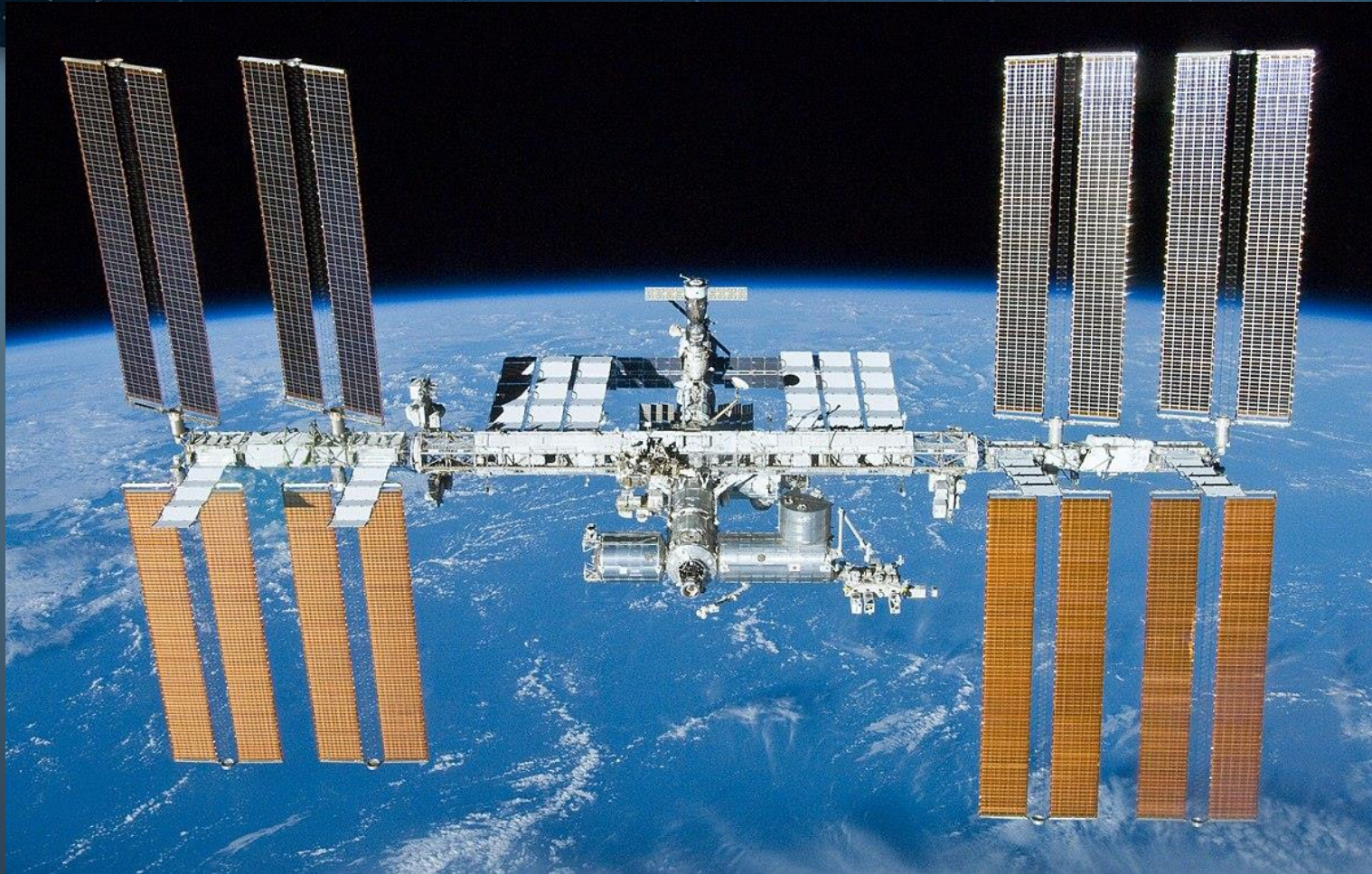
# Results



Reflectance measurements were taken on lightly compressed pellets of the untreated and indium oxide treated Z93P pigment and show approximately one percent reflectance differences across the solar spectrum



# ISS Opportunity





# MISSE-FF



The Materials ISS Experiment Flight Facility (MISSE-FF) with MISSE Sample Carriers (MSCs) in the fully open position exposing samples/experiments to the harsh environment of space in low-Earth Orbit (LEO). Image courtesy of Alpha Space.



An earlier MISSE mission

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## NASA Wallops



Nov. 8, 2018

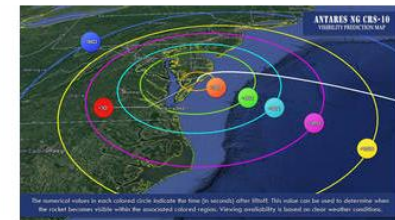
# Catch the Nov. ~~15~~<sup>16</sup> Antares Launch from Wallops

Get up early Nov. 15 to view the Northrop Grumman's Antares rocket launch from the Mid-Atlantic Regional Spaceport at NASA's Wallops Flight Facility.

The NASA Wallops Flight Facility and Virginia's Mid-Atlantic Regional Spaceport are set to support the launch of the Antares rocket, carrying the company's Cygnus cargo spacecraft to the International Space Station at 4:49 a.m. EST, Nov. 15.

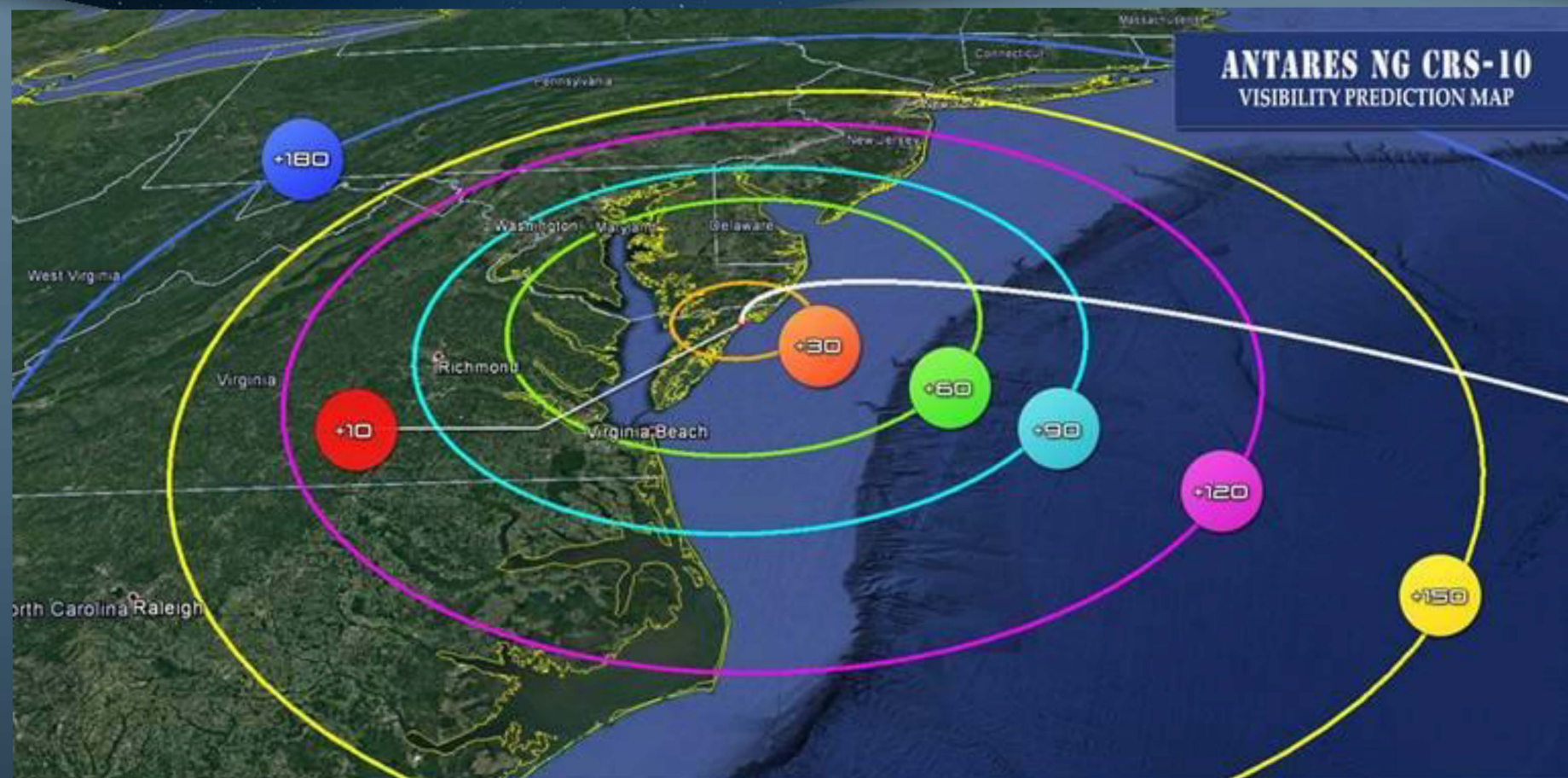
The launch may be visible, weather permitting, to residents throughout the East Coast of the United States.

The NASA Visitor Center at Wallops opens at 1 a.m. on launch day for public viewing. Additional locations for catching the launch are Robert Reed Park on Chincoteague Island or Beach Road spanning the area between Chincoteague and Assateague Islands. Assateague Island National Seashore/Chincoteague National Wildlife Refuge in Virginia will **not** be open for viewing the launch.



Viewing map for the U.S. East Coast of the upcoming NG-10 Antares launch from NASA's Wallops Flight Facility. Much of the East Coast should be able to see the rocket if the skies are clear.  
**Credits: Northrop Grumman**





The numerical values in each colored circle indicate the time (in seconds) after liftoff. This value can be used to determine when the rocket become visible within the associated colored region. Viewing availability is based on clear weather conditions.



# Acknowledgments



Adomaitis Research Group



Mark Hasegawa

